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Structural Characterization of Thin Aluminum Oxide -  
Hydroxide Layers by the Aluminum and Oxygen X-Ray Emission Bands

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Structural Characterization of Thin Aluminum Oxide-Hydroxide  
Layers by the Aluminum and Oxygen X-ray Emission Bands

by

G. A. Savanick, P. Gigl, and E. W. White

ABSTRACT

A new technique is outlined for the characterization of thin films of crystalline and amorphous aluminum oxides, aluminum oxyhydroxides and aluminum hydroxides. Shifts in Al  $K\beta$  and  $OK\alpha$  X-ray emission lines of known examples of these compounds are presented and are used to identify unknown Al-O-OH compounds.

INTRODUCTION

Characterization of aluminum oxides, aluminum oxyhydroxides and aluminum hydroxides can present serious problems when they are poorly crystallized and especially when they occur as thin layers on metal substrates. This study was undertaken to establish the feasibility of using shifts in the aluminum K-emission band (Al  $K\beta$ ), and the oxygen K-emission band ( $OK\alpha$ ) to determine the short range structure of various corrosion products on aluminum and its alloys. It has been well established that K-emission bands of the second and third period elements undergo significant changes among various compounds but consistent rules governing such changes have not been established. It is the purpose of this investigation to establish the feasibility of developing an empirical technique for identifying Al-O-OH phases.

In the case of anhydrous aluminum oxides and aluminosilicates it has been shown that Al K $\beta$  shifts depend on the number of oxygens coordinating the Al<sup>3+</sup> and also on the mean Al-O distance in a given structure.<sup>1</sup> More recently a study was undertaken on some of the compounds in the Al-O-OH system using the Al K $\alpha$  line but the results were not very definitive<sup>2</sup>. The principal result of that study was to establish for the first time the characteristic difference in the Al K $\beta$  peak from  $\alpha$  and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The oxygen K-emission band has been studied in considerable detail by at least three investigators but their results have not led to a quantitative interpretation of the shifts<sup>3,4,5</sup>. The most recent of these studies indicated that bond character may be the most common factor contributing to changes in the OK $\alpha$ <sup>5</sup>.

#### EXPERIMENTAL

A set of reference standards for the common Al-O-OH compounds were assembled and carefully characterized to confirm their structure and composition. These compounds included  $\alpha$ - and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, boehmite [Al-O(OH)], diasporite [Al-O(OH)], gibbsite [Al(OH)<sub>3</sub>] and bayerite [Al(OH)<sub>3</sub>]. These standards were studied in the form of thin (two to five micron thick layers) deposited from dilute suspension onto polished beryllium.

An ARL model EMX electron microprobe operated at 20 keV and 0.1  $\mu$ A specimen current was used to excite and analyze the x-ray spectra. An electron beam diameter of about 100  $\mu$ m was used in order to minimize specimen damage. A four inch radius curved crystal spectrometer, geared to read wavelength directly for an ammonium dihydrogen phosphate (ADP) crystal was used with a thin formvar window flow proportional counter.

An ADP crystal ( $2d=10.64\text{\AA}$ ) was scanned at  $0.01\text{\AA}/\text{min}$  to diffract the first order Al  $K\beta$  line. A clinochlore crystal ( $2d=28.36\text{\AA}$ ) was scanned at  $0.0267\text{\AA}/\text{min}$  to diffract the oxygen  $K\alpha$  line. The resolution of the ADP crystal is approximately  $1000 \left(\frac{\lambda}{\Delta\lambda}\right)$  at  $8\text{\AA}$  and the clinochlore crystal has a resolution of about 500 at  $28\text{\AA}$ . Al  $K\beta$  peak count rates were in the range of 50 to 150 counts per second while the OK peak count rate varied from 100 to 250 counts per second. The peak positions were measured at two-thirds height and could be reproduced within  $\pm 0.0003\text{\AA}$  for Al  $K\beta$  and  $\pm 0.001\text{\AA}$  for O  $K\alpha$ .

#### RESULTS AND DISCUSSION

The spectra recorded in this study are reproduced in Figures 1 and 2. Data on changes in peak position and line widths are tabulated in Table 1. The values are tabulated as changes in peak position measured at  $2/3$  height. Each value in the table is average for five separate measurements. Figure 1 is a composite of the Al  $K\beta$  lines for the pure compounds. This figure shows that a broad doublet ( $6\text{eV}$ ) at half-height is characteristic of  $\alpha\text{-Al}_2\text{O}_3$  (corundum) while all other peaks are observed as singlets at this level of resolution. The peak positions and profiles of the two Al O(OH) compounds boehmite and diaspor—are significantly different. Likewise, the peak positions and profiles of gibbsite and bayerite, the two  $\text{Al}(\text{OH})_3$  compounds, are distinctly different. The peak from  $\gamma\text{-Al}_2\text{O}_3$  occurs at the longest wavelength of the singlet peaks.

Figure 2 is a composite of the oxygen K-emission bands obtained from the same standards. This figure shows that each emission band appears as a fairly sharp peak with a well resolved long wavelength tail. Boehmite, diaspor—and  $\alpha\text{-Al}_2\text{O}_3$ , are not significantly different at this level of resolution. The peaks from gibbsite and bayerite resemble each other but occur at a distinctly higher energy than those from the other materials. In addition, the long wavelength tails from

Table I  
 Summary of Peak Shifts ( $\Delta\lambda$ ) Measured at 2/3 Peak Height

Standard	Formula	$\Delta\text{AlK}\beta$ ( $\text{\AA} \times 10^4$ )	$\Delta\text{OK}\alpha$ ( $\text{\AA} \times 10^4$ )
Corundum	$\alpha\text{-Al}_2\text{O}_3$	0	0
	$\gamma\text{-Al}_2\text{O}_3$	-1	-32
Diaspore	Al O (OH)	-16	0
Böhmite	Al O (OH)	-8	+3
Gibbsite	Al (OH) <sub>3</sub>	-15	-88
Bayerite	Al (OH) <sub>3</sub>	-12	-77

gibbsite and bayerite are shifted toward higher energies.

The oxygen spectra in Figure 2 are not as well resolved as those reported recently by Chun and Hendel<sup>5</sup>. However, it is advantageous to use the electron microprobe to study oxygen peak shifts because they can be recorded quickly (15 minutes per scan) on a linear intensity scale and only a very small sample is required.

Figures 1 and 2 can be used to positively identify unknown aluminum oxide-hydroxide compounds provided the unknown is a single phase of one of the six dealt with in this study.

A broad doublet Al K $\beta$  peak is characteristic of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The Al(OH)<sub>3</sub> compounds can be distinguished from the other compounds by their short wavelength oxygen peak and once this distinction is made they can be distinguished from each other on the basis of the position of the Al K $\beta$  peak. The Al K $\beta$  peak of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is distinctive in that it occurs at the longest wavelength side of the single Al K $\beta$  peaks. The Al K $\beta$  peak from diasporite is significantly narrower than that from boehmite.

The Al K $\beta$  and OK $\alpha$  result from electronic transitions from the valence band to the ionized K-shell. Since the electronic configuration of Al<sup>+3</sup> and O<sup>-2</sup> is identical it seems reasonable to expect that the Al K $\beta$  and OK $\alpha$  would have the same form if the Al<sup>+3</sup> and O<sup>-2</sup> valence electrons were populating the same energy level. However, there is a great disparity in the width of the Al K $\beta$  band (up to 6eV) as compared with that of the OK $\alpha$  band (ca 1.5eV). This suggests that the oxygen valence electrons and the aluminum valence electrons form independent valence bands and are not homogenized into one valence band characteristic of the entire solid.

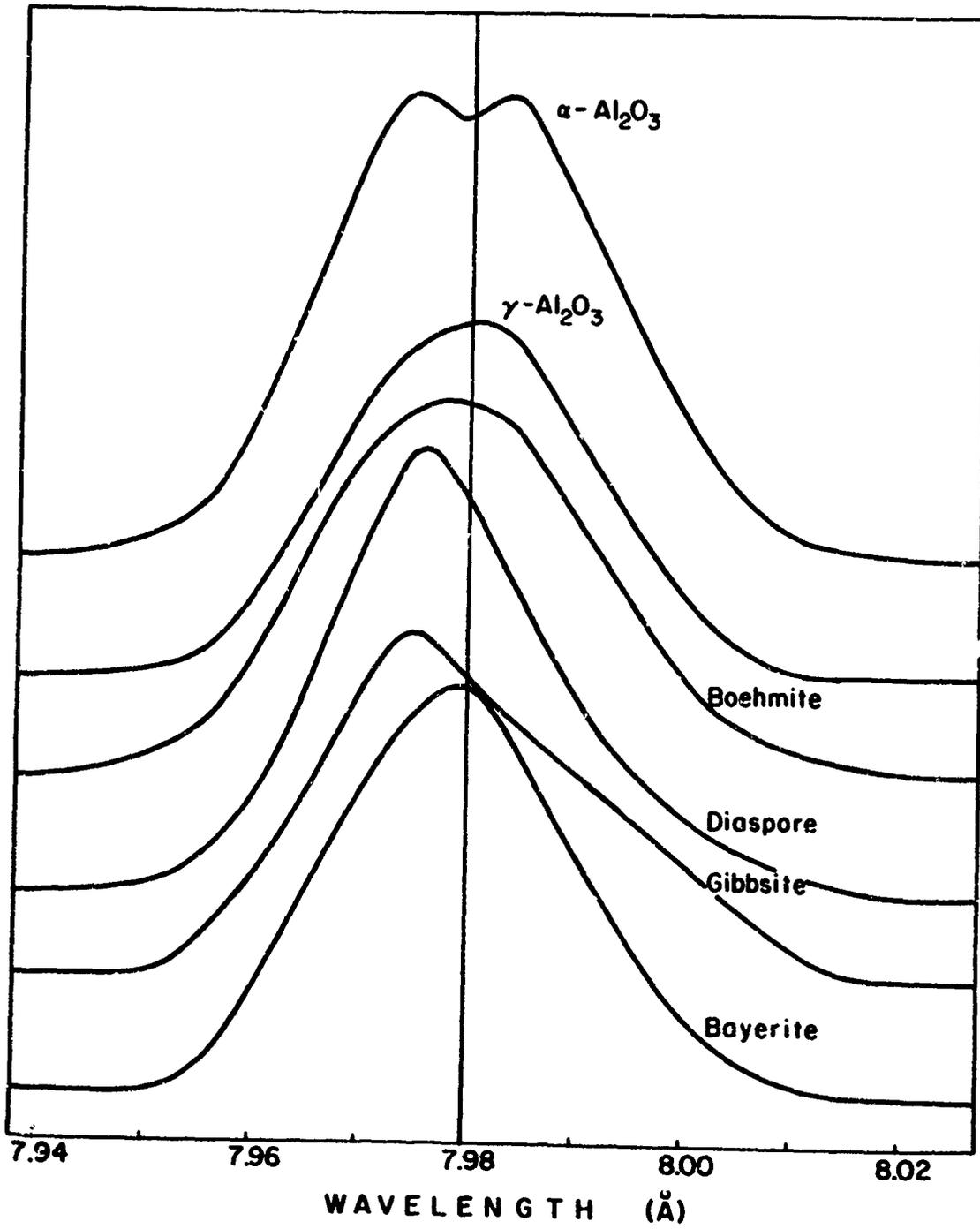


Fig. 1 AlK $\beta$  peaks of aluminum-oxide-hydroxide compounds

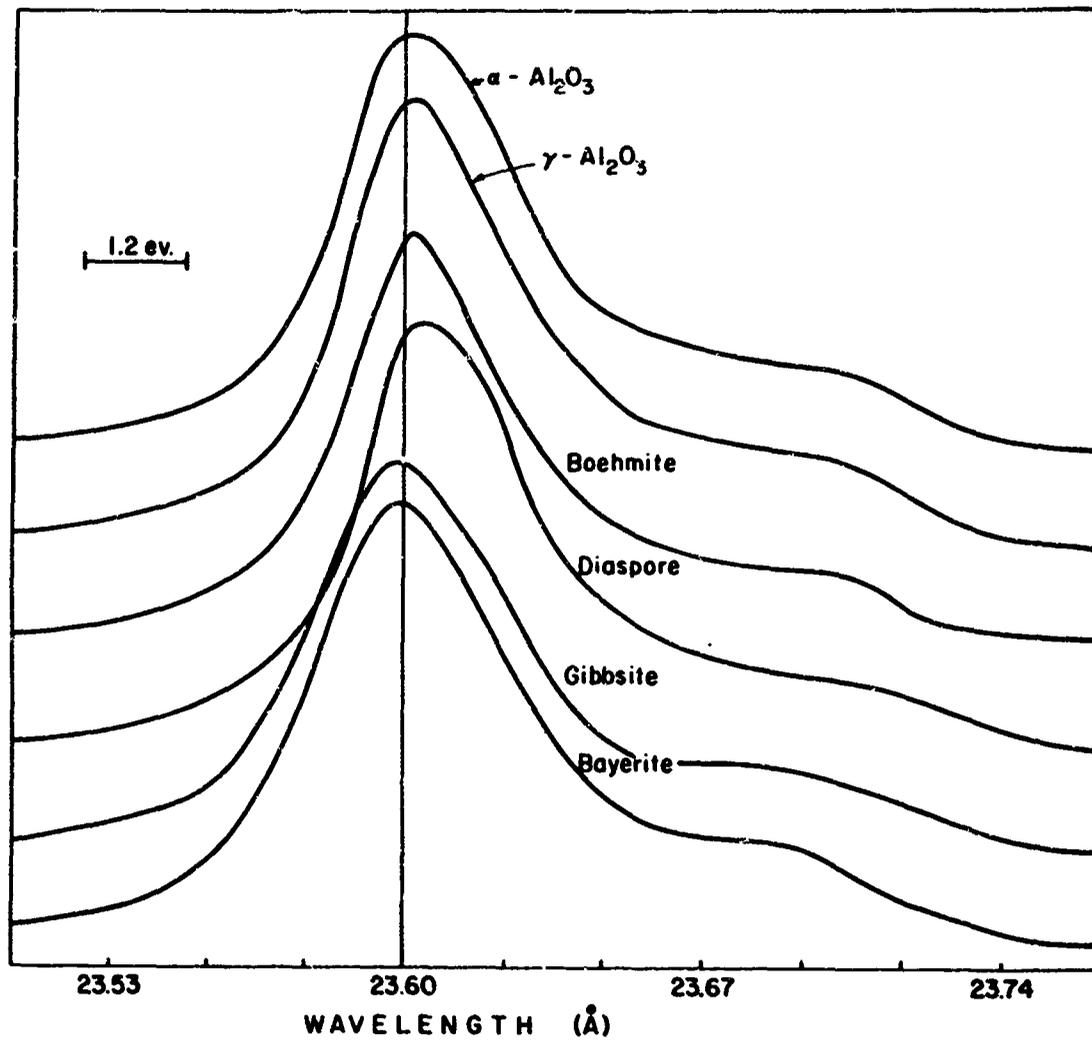


Fig. 2  $OK\alpha$  peaks of aluminum-oxide-hydroxide compounds

The formation of separate energy level diagrams for each type of atom present in an insulator solid is a well-known phenomenon (Parratt). Cross transitions of electron from the aluminums to oxygen and visa versa are probably of no consequence in the wavelength region included in this study. In fact, cross transitions are generally not dominant features in soft x-ray spectra (Parratt).

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